Perchlorate from Safety Flares
A Threat to Water Quality

Miguel A. Silva, 10/23/03

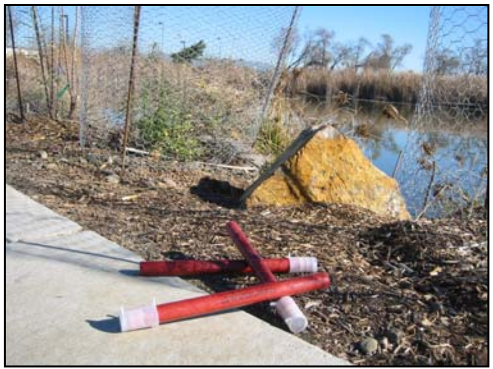

Fig. 1 – Incendiary Safety Flares.

INTRODUCTION

The Santa Clara Valley Water (District) has perfomed two series of flare tests, known as "Flare in the Barrel" tests designed to measure the leachibility of perchlorate from highway/emergency safety flares (fusee) in water. The objective of these tests is to understand the potential for combusted (burnt) and uncombusted (unburnt/unspent) flares used ubiquitously on roadways to impact nearby surface and ground water quality following a rain event with perchlorate contamination. These tests help answer questions such as:

> *Can flares cause perchlorate contamination in water?*
> *If so, what is the potential impact?*
> *Is there a difference in contamination contribution between burnt vs. unburnt flare?*

BACKGROUND

The District has become increasingly concerned regarding recent increased detections of perchlorate (ClO_4-) in our groundwater basins. Sources of perchlorate include rocket fuel, highway safety flares, fireworks, matches, dyes, lubricating oils, air bag inflators, paints, electro painting, and medical specialty tests (see SCVWD Perchlorate Fact sheet[1]).

Studies have shown perchlorate to be an endocrine disruptor by blocking iodine intake in the thyroid gland, leading to thyroid hormone related adverse health effects (including neurological impairment, hypothyroidism, and in rare cases thyroid cancer), especially in highly thyroid gland sensitive groups such as pregnant mothers, fetuses, and young children[2].

Perchlorate is a chemical used in rocket fuel and other explosive products. It disrupts iodine intake in the thyroid gland, which regulates hormone functions. Some studies suggest it may be a cause of thyroid cancer. Pregnant women and infants are at highest risk because perchlorate may impair neurological development in fetuses and small children.

Olin Corporation, a former highway safety flares/fusee manufacturer in Santa Clara County has been implicated to a perchlorate contaminated groundwater plume extending at least 9 miles long and affecting hundreds of private drinking water wells with low levels of perchlorate in the cities of Morgan Hill & San Martin, CA.

Inventory records gathered by the District indicate more than 40 metric tons of flares were used/burnt in 2002 alone in Santa Clara County. Theoretically[3], a single 20-minute flare can potentially contaminate up to 2.2 acre-feet of drinking water to just above California Department of Health Services' current Action Level of 4 µg/L.

Chemical composition of flares reported by manufacturers primarily include strontium nitrate (75% by weight), potassium perchlorate (<10%), sulfur (<10%), sawdust/oil (<10%). Other ingredients in lesser amounts include: synthetic rubber, aromatic polycarboxylic anhydride fuel, benzene tetracarboxylic acid (dianhydride and metallic dianhydride), sodium nitrate, polyvinyl chloride case binder, dextrin, magnesium, cellulose nitrate (nitrocellulose charcoal), black powder, uintaite, wax, and red phosphorous.

EXPERIMENTAL PROCEDURE

To simulate outdoor flare-water contact, five different scenarios (referred to as modules) were configured as shown in Table 1.

Each module/bucket consisted of deionized water (15 L) in a continuously mixed environment. Water stability parameters were collected periodically during the 3.5 hr. flare-water contact test, consisting of temperature, pH, and electrical conductivity. Afterwards, a water sample was collected and analyzed for dissolved perchlorate as ClO_4- (EPA Method 314.0) and nitrate as NO_3- (EPA Method 300).

The burning of the flares was performed in a dry environment on top of aluminum metal sheets. The flare material was weighted before and after each burn. The metal sheets were used to hold and collect the flare debris/ashes before mixing their contents onto their respective bucket containing 15 L of deionized.

OBSERVATIONS & DISCUSSION

Series 1

A yellowish-tan saw-dust/cardboard was observed inside the unburnt flares during the slicing and submergence of the flares. Small sized solids floated to the top of the water surface during flare submergence, covering the entire surface of the water, while the larger sized solids easily sank to the bottom of barrel during mixing for M1 and M3. Aside from the floating sawdust, the water remained relatively clear in M1 & M3 as compared to M2 and M4. The water from M2 and M4 was noticeable cloudier with suspended ash debris. A white milky viscous substance was observed at the bottom of M2, M3 and M4 (ignited flares). Continuous mixing was maintained in all barrels during testing.

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[1] Santa Clara Valley Water District Perchlorate Factsheet can be found at http://www.valleywater.org

[2] Public Health Goal for Perchlorate In Drinking Water (Draft), Cal EPA, December 2002

[3] Assumes worse-case-scenario of 100% homogenous full mixture and 0% mass losses (chemical, transport, degradation, environmental, etc...), of a 20-minute flare (217g) composed of up to 10% potassium perchlorate by mass (CA Action level likely to increase to 6 µg/L).

Table 1 – Series 1 & 2

Test No.	Flare Description[4]	Simulation
M1	0% burnt + sliced open	Represents conditions of unburnt, followed by partial destruction (run over by motor vehicles) flare in contact with rainfall.
M2	50% burnt + unaltered	Represents conditions of 50% flare burnt during dry conditions, experiencing no other damage (in contrast to M3), followed by rainfall.
M3	50% burnt + sliced open	Represents conditions of 50% flare burn during dry conditions, followed by run over by motor vehicles, then rain fall.
M4	100% burnt + sliced open	Represents conditions of 100% flare bunt during dry conditions, followed by partial destruction/run-over by vehicles, followed by rainfall.
M5	control blank (no flare)	Represents clean water having no contact with flares intended to quantify experimental error resulting from cross-contamination.
M6	100% burnt + sliced open	Represents conditions of 100% flare bunt during dry conditions, followed by partial destruction/run-over by vehicles, followed by rainfall. This is comparable to M4 (repeat).
M7	90% burnt + sliced open	Represents conditions of 90% (18 minutes) flare burnt during dry conditions, experiencing being run over by vehicles, followed by rainfall.
M8	67% burnt + sliced open	Represents conditions of 67% (13.5 minutes) flare burnt during dry conditions, experiencing being run over by vehicles, followed by rainfall.
M9	0% burnt + NO WATER (Solids Analysis)	Represents flare (20-minute) for solids analysis of perchlorate and nitrate without any submergence/dilution with water.
M10	Control blank	Represents clean water having no contact with flares intended to quantify experimental error resulting from cross-contamination. This compares to M5.
M11	Triple blind blank	Independent laboratory spiked perchlorate sample. ID No. 0204-03-03.1

A problem observed with the first simulation tests, was that suspended solids easily adhered to the surface of the probes used to collect water stability readings. The debris was, of course, rinsed and cleaned-up before collecting data from the next barrel. This practice, however, may have nonetheless introduced some error and cross contamination as evidence of the 50 *µg/L* of perchlorate detected in the blank barrel (M5). Although the 50 *µg/L* "experimental error" was less than 0.03% for the full range of results, it was decided to conduct additional testing with more stringent QA/QC controls.

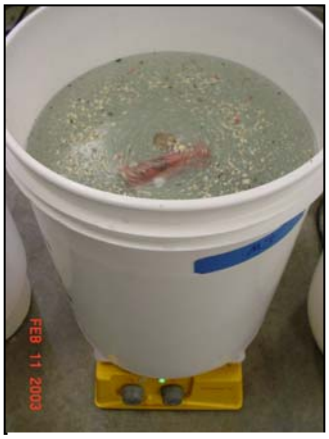

Fig. 2 – Floating flare debris

Series 2

The second experiment (Table 2) was carried out with four main differences (1) the contact time was increased to 24 hours; (2) water stability probes were NOT immersed in the flare-water solution prior to collecting water samples for perchlorate and nitrate analysis so as to avoid cross contamination; (3) a triple blind blank was used with a known amount of perchlorate; and (4) the certified analytical laboratory was changed – see Table 2.

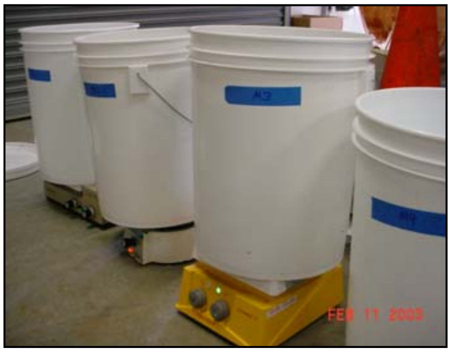

Fig. 3 – Test modules on magnetic stirs

RESULTS

Refer to Figures 6-12 for details.

Perchlorate

The highest dissolved perchlorate concentration occurred from unburnt flare, up to 243,000 µg/L for M1; the lowest occurred with M4, the fully burnt flare with 103 µg/L of perchlorate (excluding blanks). In just 3.5 hrs. 51% of maximum perchlorate available (based on perchlorate solids analysis) per flare had leached out of the unburnt flare.

The sliced flare (M3) contaminated water with perchlorate 20 times higher

(151,000 µg/L) than the unsliced flare (M2) with 7,800 µg/L (both flares 50% burnt).

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[4] All flares (20-minute) were burnt in dry environments and therefore do not account for significant mass losses to the atmosphere that would not occur during the burning of a flare during an actual rain fall event.

Table 2 – Results Summary

Test Series	Test No.	ºC	E.C. (mS/cm)	pH	Perchlorate (µg/L)	Nitrate (mg/L)
Series No. 1 (3.5 hrs)	M1 (0% burnt/sliced)	19.0	5	8.7	243,000	5,920
	M2 (50% burnt/unaltered)	19.6	1.7	11.9	7,800	94.3
	M3 (50% burnt/sliced)	19.1	4.0	11.8	151,000	3,250
	M4 (100%burnt/sliced)	19.2	2.8	12.3	103	12
	M5 (control blank – no flare)	18.6	0.004	8.6	48	<2
Series No. 2 (24 hrs.)	M6 (100% burnt/sliced)	16.0	4.1	12.4	130	14
	M7 (90% burnt/sliced)	15.6	4.6	12.3	6,300	-
	M8 (67% burnt/sliced)	14.8	5.9	12.1	160,000	-
	M9 (0% burnt/no water) (solids analysis)	-	-	-	50,000,000 (µg/Kg)	450,000 (mg/Kg)
	M10 (control blank)	15.1	0.003	6.9	<4	-
	M11 (triple blind blank)	-		-	7.5	-

Additional flare-water contact time (to 24 hrs) resulted in 26% increase in dissolved perchlorate concentration for the 100% burnt flares, i.e. 103 to 130 µg/L for M4 and M6, respectively.

A 90% burnt flare (M7) resulted in 63,000 µg/L perchlorate contamination (i.e. over 480 times that of a 100% burnt flare (M6).

A 2/3 burnt (67%) flare (M8) resulted in 160,000 µg/L perchlorate contamination (i.e. 1,230 times that of a 100% burnt flare (M6).

A solids analysis on a flare confirm composition to be 6.6% (calculated) potassium perchlorate [$KClO_4$] by dry weight per flare (M9), i.e. 50,000,000 µg/Kg as (measured) perchlorate.

Nitrate

Dissolved nitrate concentrations from flares generally follow similar patterns to perchlorate, for example, 100% burnt flares, resulted in 12 and 14 mg/L for M4 and M6. A perchlorate solids analysis on a flare confirm flare composition of 76.6% (calculated) strontium nitrate [$Sr(NO_3)_2$] by dry weight per flare (M9), i.e. 450,000 mg/Kg (measured) as nitrate.

pH

The water in contact with burnt flares (M2, M3, and M4) showed an increased pH level from 7.0 to over 11.6 after 3.5 hrs of contact time. In contrast, the unburnt flare (M1) maintained a pH of 8.9, similar to the control blank M5.

A longer contact time (24 hrs) resulted in even higher pH values than the 3.5 hrs contact time for all the burnt flares (final pH value of 12.4, 12.3, and 12.1 for M6, M7 and M8). The control blank stayed at a pH of 6.9.

Electrical Conductance

During the 3.5 hrs flare-water contact, the unburnt flare (M1) generated the highest amount of electrical conductance of up to 5 mS/cm. While, the unsliced half-burnt flare (M2) generated the lowest conductance of 1.7 mS/cm. The sliced flare (M3) achieved over twice (2.5 times) the conductivity of an unsliced flare (M2). Generally, the more dissolved perchlorate and nitrate salt concentrations the higher the electrical conductance obtained.

Additional flare-water contact time (24 hrs) consistently resulted in higher electrical conductance than the 3.5 hrs. For 100% burnt flares, an increase of 37% electrical conductance was observed (from 3.0 mS/cm to 4.1 mS/cm for M4 and M6, respectively), despite experiencing colder water temperatures. M7, M8 and M10 (control blank) resulted in electrical conductances of 4.6, 5.9 and 0.0003 mS/cm, respectively.

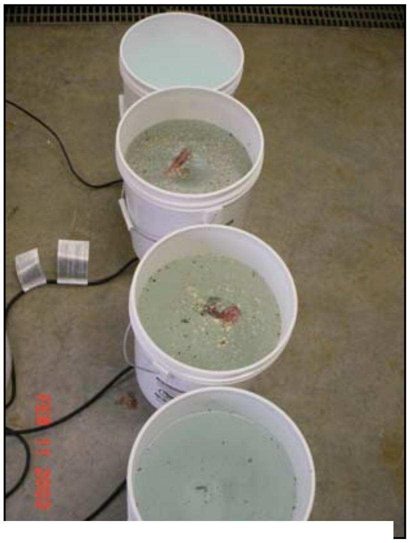


Fig. 4 – Modules M-6, M-7, M-8, and M-10 (bottom to top).

Temperature

No significant changes in temperature were observed during Series No. 1. Series No. 2 had final (after 24 hrs contact time) temperatures about 5 degrees (centigrade) colder than Series No. 1, averaging at 15ºC.

CONCLUSIONS

(1) Incendiary flares can be a significant source of perchlorate contamination to both surface and groundwater.

(2) Unburnt flares improperly disposed of can contaminate water with perchlorate up to 2,000 times more than 100% burnt flares.

RECOMMENDATIONS AND FUTURE TESTING

Additional studies are recommended to understand basic fate and mass transport mechanisms governing the extent of perchlorate contamination from safety flares to surface and groundwater supplies. Specific recommendations include the following:

(1) The non-point source patterns of perchlorate should be studied, particularly near areas of high automobile accidents (high flare usage) that are near infiltration devices (such as dry wells, storm drains, etc.) to surface and groundwater supplies.

(2) Best management practices/policies should be developed regionally to minimize use of safety flares and thereby prevent contamination. Such practices can include proper disposal (especially unburnt debris), additional user training, and the use of safety-flare alternatives (such as pulsating Light Emitting Diodes - LEDs) particularly near vulnerable areas.

(3) Sensitive groundwater supply areas should be well identified and adequately protected (for example, unconfined shallow groundwater supplies with direct infiltration).

ACKNOWLEDGMENTS

This report was made possible by the valuable contributions of James S. Crowley, P.E.,Thomas Mohr, RGE, Lane Davis, Cris Tulloch, and Meow Sim of SCVWD.

Figures 6 through 12 follow.

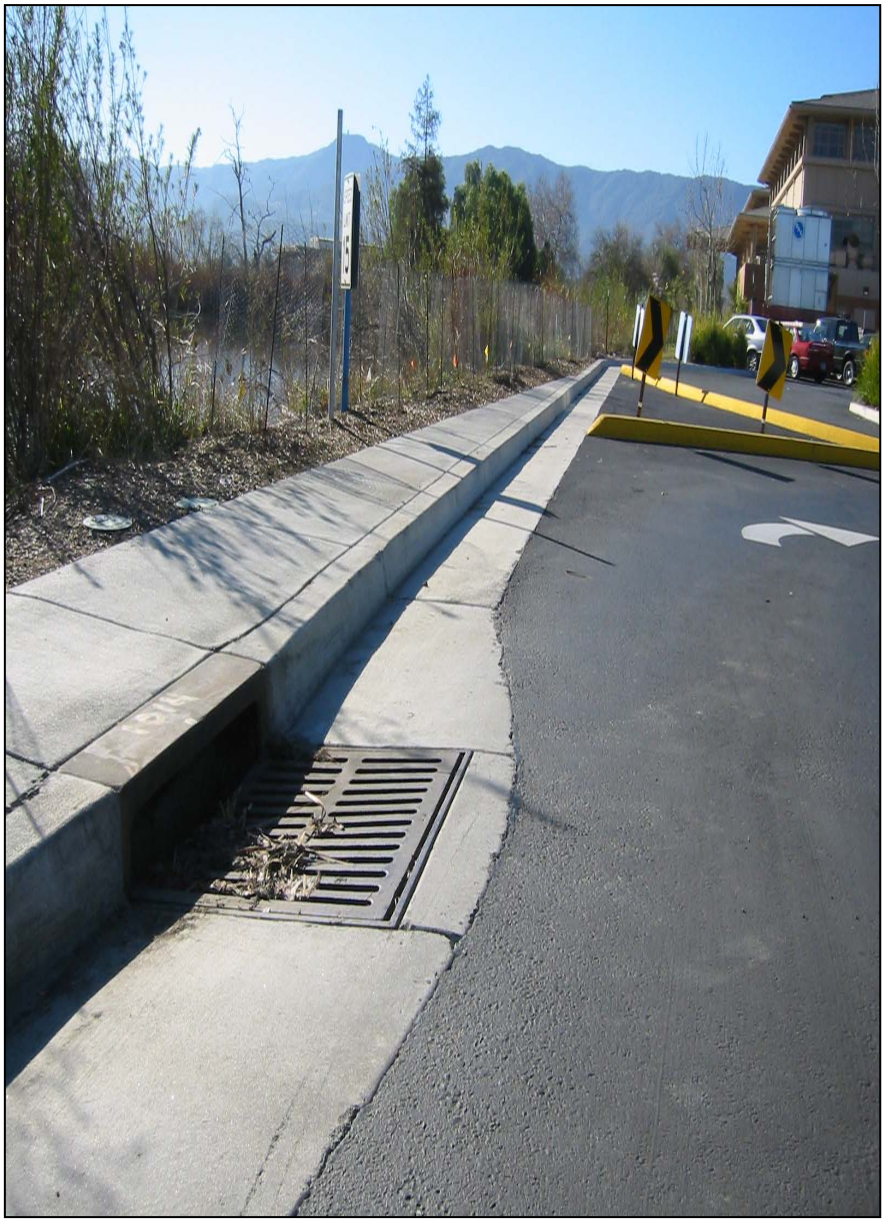


Fig. 5 – Non-point sources (run-off and storm drains/conduits).

Figure 6. Flare-in-the-Barrel Test - pH Stability Curves

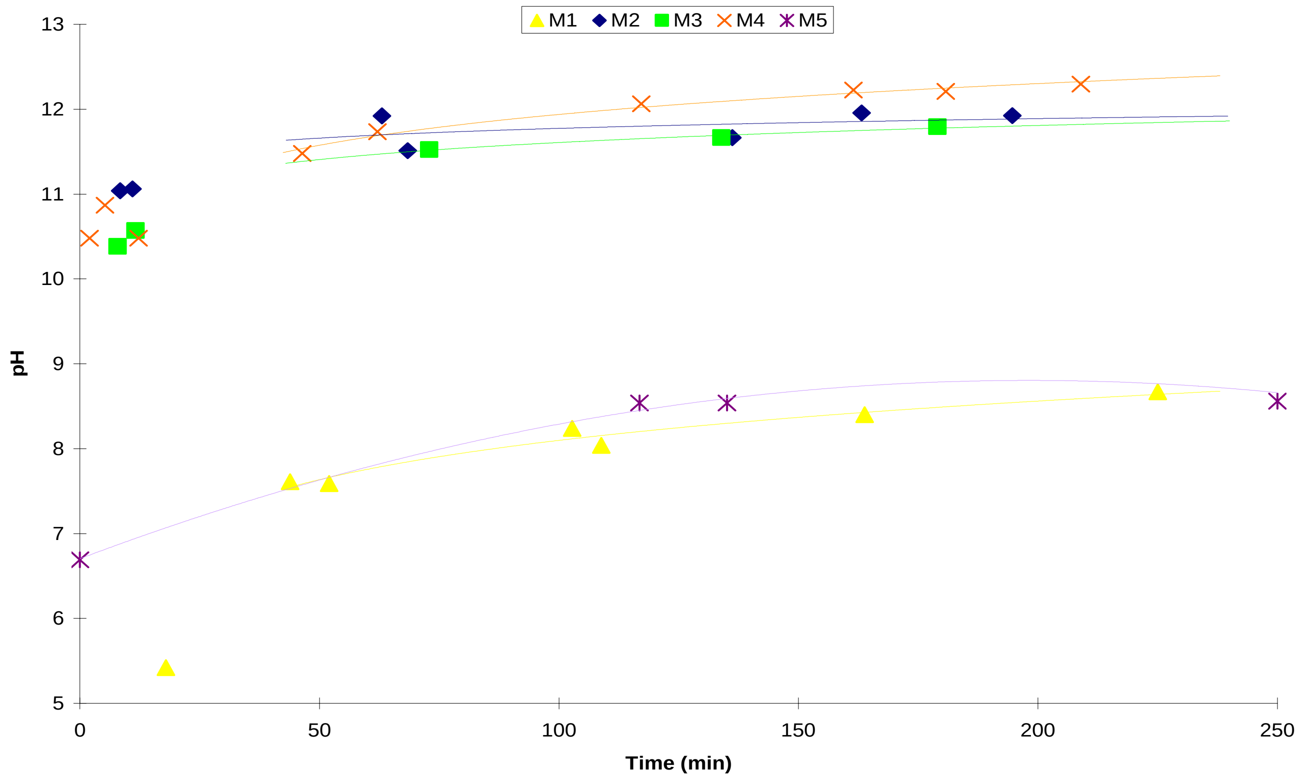


Figure 7. Flare-in-the-Barrel Test - **Electrical Conductance Stability Curves**

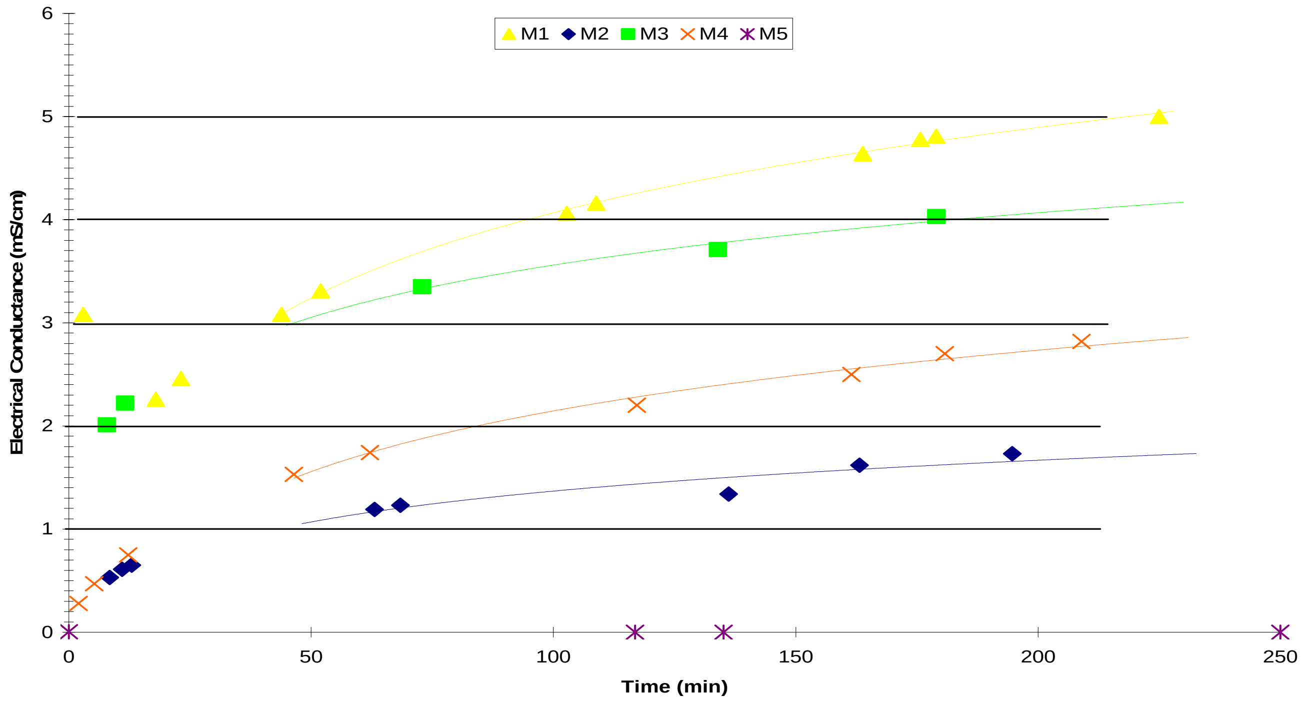


Figure 8. Flare-in-the-Barrel Test - Temperature Stability Curves

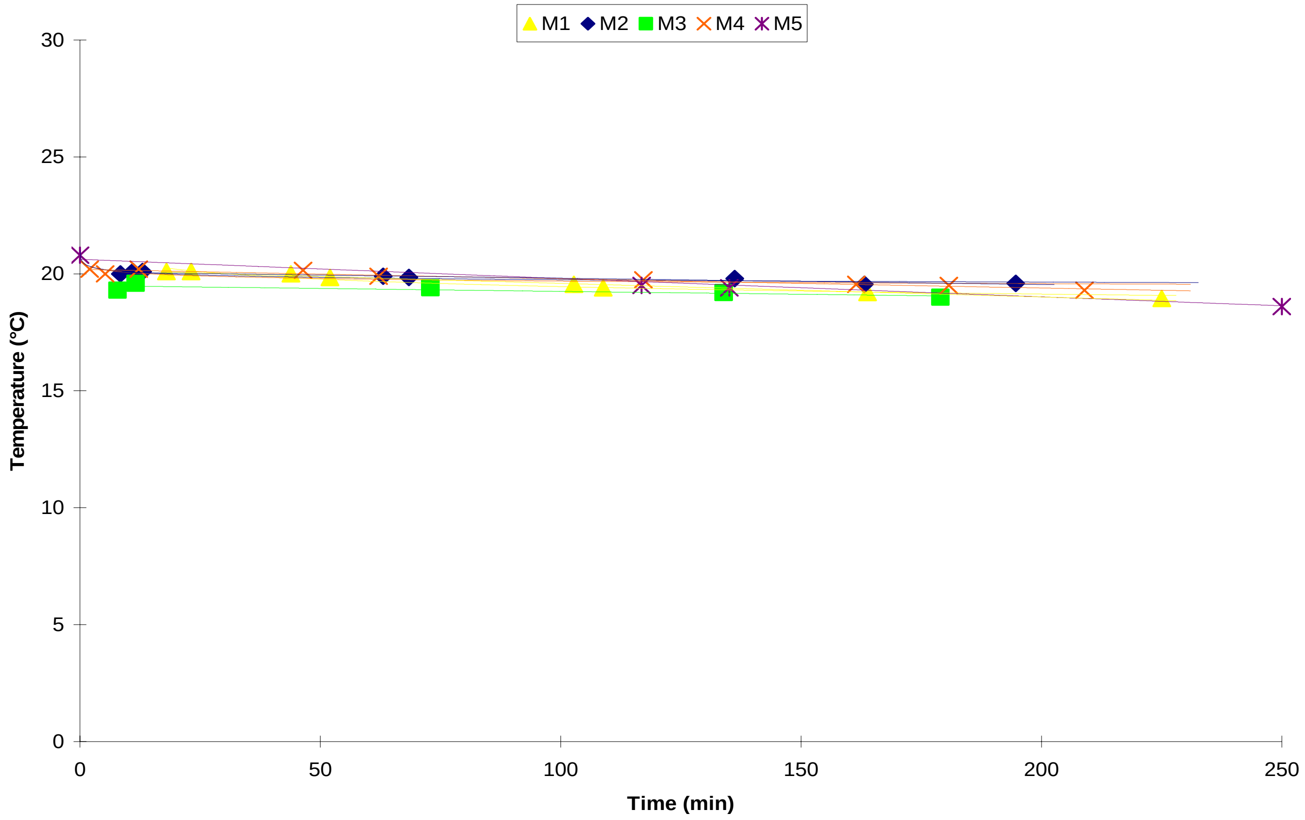


Figure 9. Flare-in-the-Barrel Test (3.5 Hr.) - Perchlorate Concentration Results

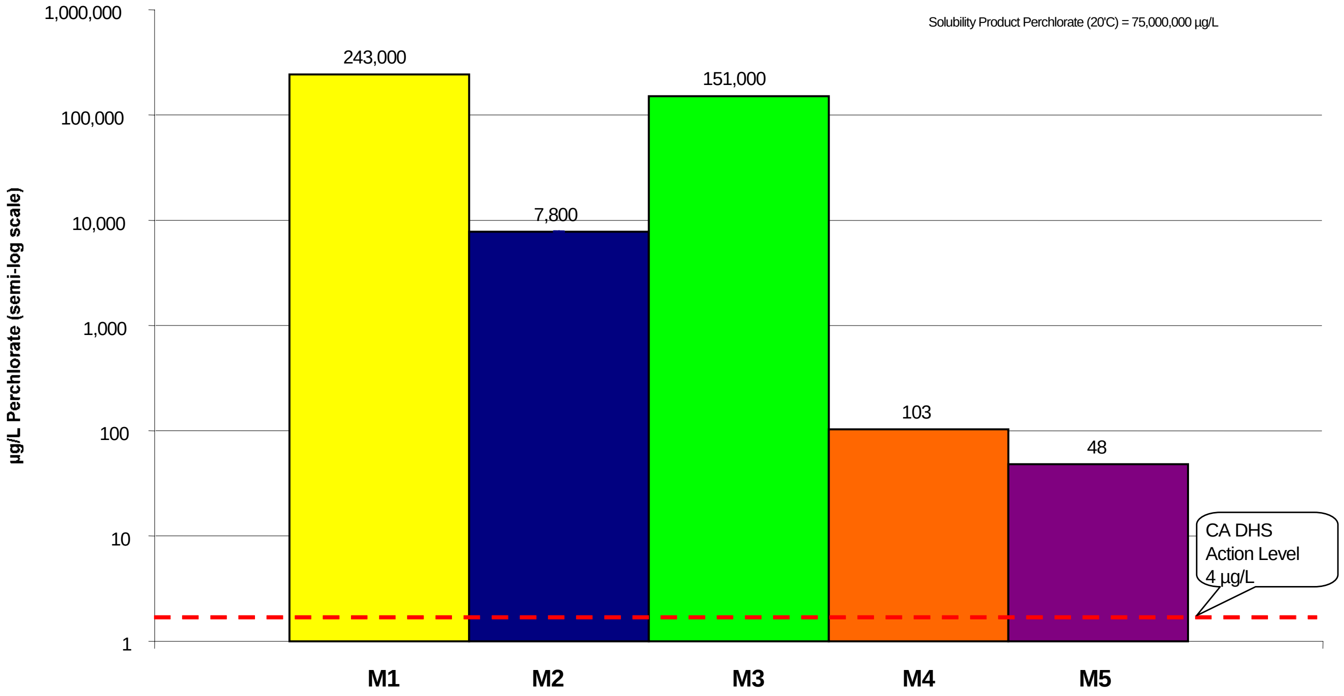


Figure 10. Flare-in-the-Barrel Test (24 Hr.) - Perchlorate Concentration Results

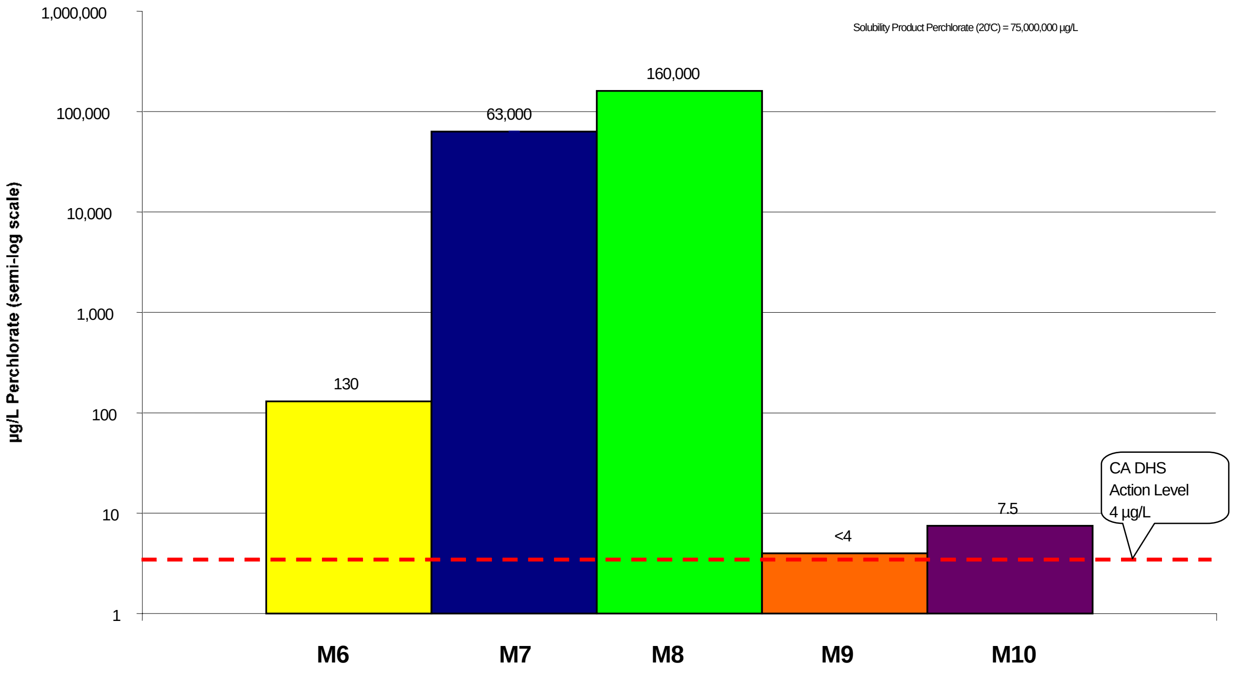


Figure 11. Flare-in-the-Barrel Test (3.5 Hr.) - Nitrate Concentration Results

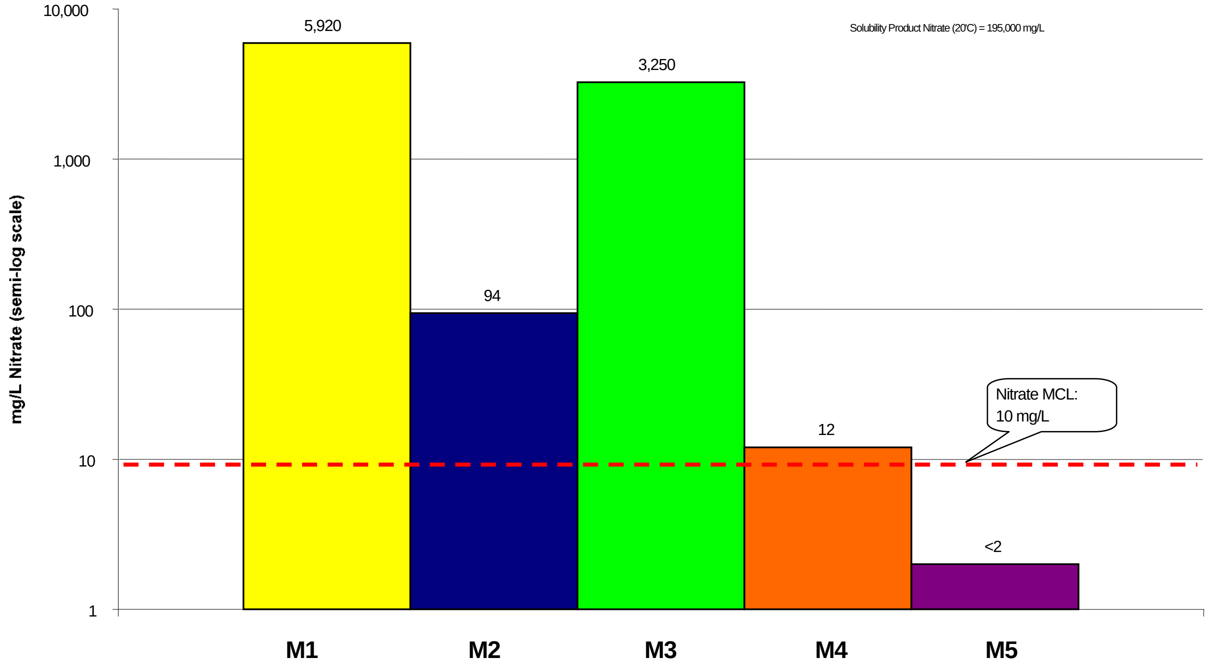
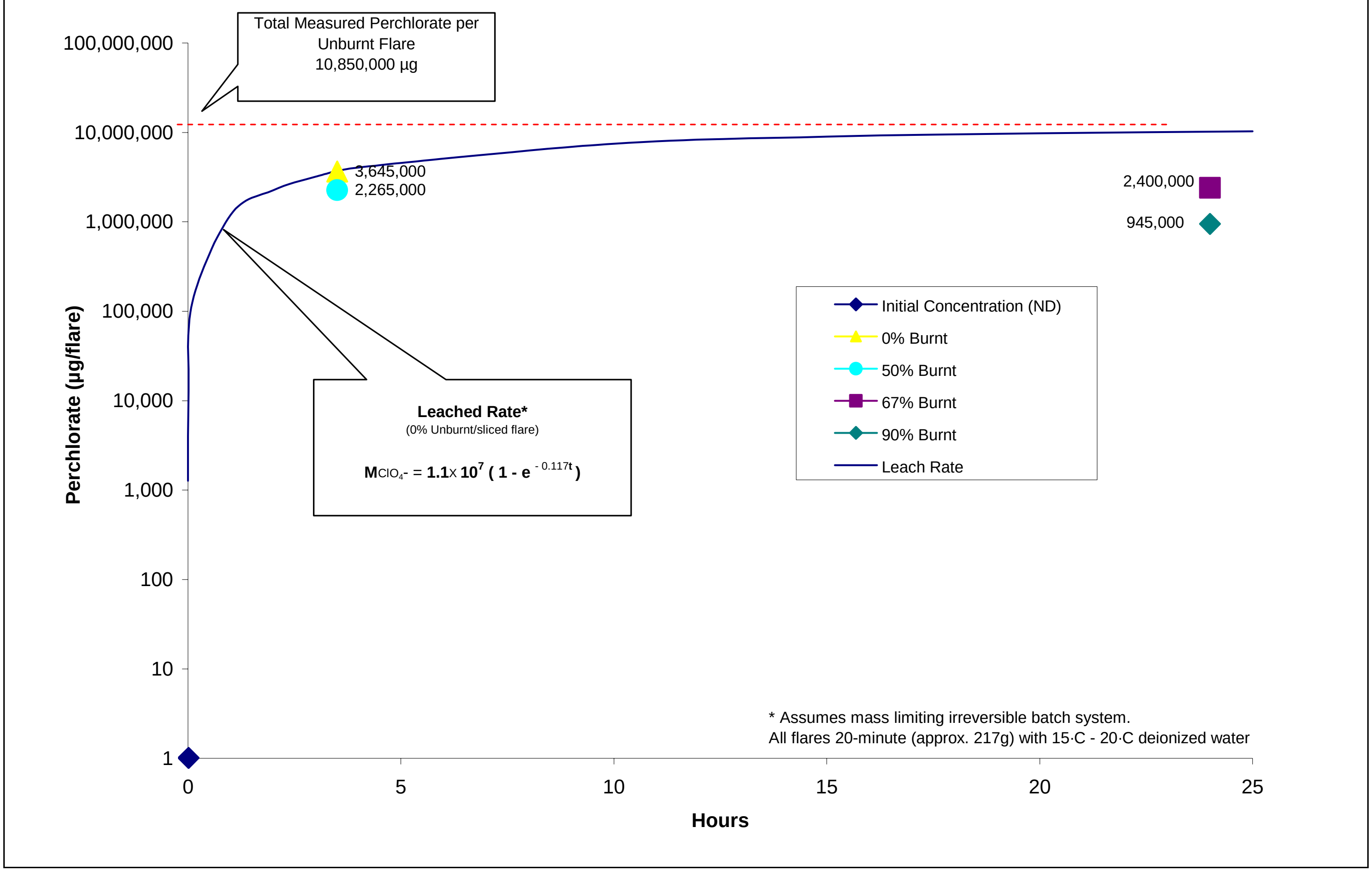


Figure 12 - Perchlorate Mass Leach Rate per Flare (sliced)



$M_{ClO_4^-} = 1.1 \times 10^7 \, (1 - e^{-0.117t})$

* Assumes mass limiting irreversible batch system.
All flares 20-minute (approx. 217g) with 15·C - 20·C deionized water